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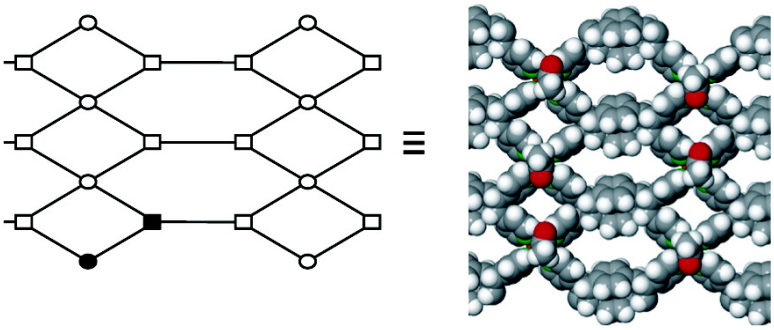

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Design and Construction of a 2D Metal Organic Framework with Multiple Cavities: A Nonregular Net with a Paracyclophane that Codes for Multiply Fused Nodes

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Metal organic frameworks (MOFs) are solids with emerging technological applications in materials science (e.g., gas storage, catalysis).[1] The strategy to construct MOFs involves self-assembly of metal ions and organic building units of predefined stereochemistry and functionality. Given the structural diversity of two- (2D) and three-dimensional (3D) MOFs, periodic nets[2,3] are now used to rationalize and define targeted MOF structures.

With this in mind, we sought to construct a 2D MOF with two different cavities. Solids with different cavities and channels have been targets of zeolites[4] and a 3D MOF,[5] while 2D MOFs continue to exhibit unique chemicophysical properties.[1] However, the process of self-assembly is considered to favor nets of highest symmetry, or *default* nets,[6] which suggested that a 2D MOF with two different cavities may be difficult to construct.

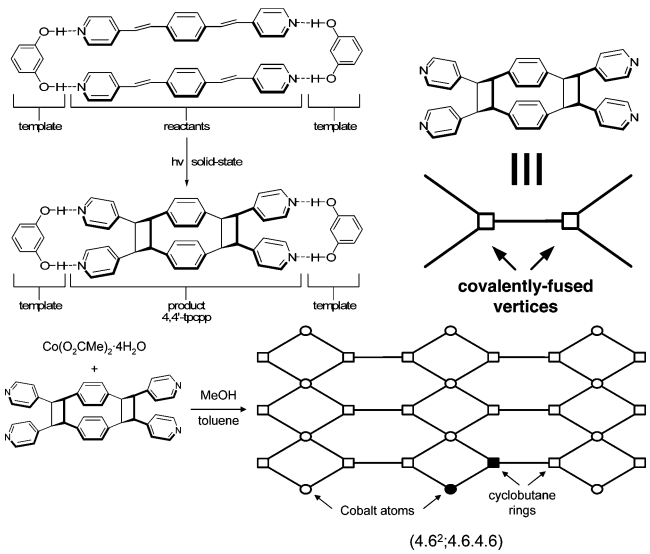
To construct a 2D MOF with two different cavities, we turned to a class of low symmetry nets known as nonregular nets.[3,7] Most 2D cavity-containing MOFs adopt topologies of either regular (i.e., tiling of identical regular polygons with identical vertices)[1] or semiregular nets (i.e., tiling of different regular polygons with identical vertices).[8] Moreover, to our knowledge, tiling of two different polygonal cavities with two different vertices, or a nonregular net,[3,7] has not been described.[9] Here, we report the design and construction of a 2D MOF with a structure that conforms to a nonregular net that is related to one of the 20 known 2-uniform nets (Scheme 1). To construct the cavity-containing MOF, we have implemented a strategy recently proposed by O'Keeffe and Yaghi, in which an organic molecule codes[6] for covalently fused nodes within the framework. The coding is employed as a means to promote the self-assembly process to give the low symmetry, or *nondefault*,[6] net structure. We believe that the strategy employed here may be used to aide the general construction of MOFs with multiple cavities.

The MOF is based on the self-assembly of an *exo*-tetradentate ligand and a Co(II) center. The ligand, tetrakis(4-pyridyl)-1,2,9,10-diethano[2.2]paracyclophane (4,4′-tppcp), is obtained from a template-directed solid-state organic synthesis,[10] and we anticipated it could act as two fused 3-connected vertices within a 2D framework. Self-assembly of 4,4′-tppcp with a source of a planar 4-connected node, such as an octahedral M(II) ion,[11] could give a 2-uniform[7,12] net with square and hexagon cavities that entrap different guests.[4,5] MOFs with walls comprised of paracyclophanes could also yield solids with selective catalytic properties, given the role of [2.2]-paracyclophanes in catalysis.[13]

Addition of 4,4′-tppcp (0.115 g, 2.0 mmol) into a pink solution of $Co(O_2CMe)_2 \cdot 4H_2O$ (0.05 g, 2.0 mmol) (1:1 ratio) in MeOH (20 mL) resulted in a pale orange−pink solution. Addition of toluene (40 mL) to the orange−pink solution produced pink crystals of composition $\{[Co(O_2CMe)_2(4,4'\text{-tppcp})] \cdot 2MeOH \cdot toluene\}_n$ (**1**·2MeOH·toluene) within a period of 2 weeks (yield: 70%).

A view of the crystal structure[14] of **1** is shown in Figure 1. As anticipated, the components have assembled to form a 2D cavity-containing MOF. Each Co(II) atom lies in an octahedral coordination environment that involves four pyridyl N-atoms from four different 4,4′-tppcp molecules at the equatorial plane and two O-atoms from two monodentate acetate ions at the axial positions. As a consequence of this arrangement, each Co(II) ion acts as a 4-connected vertex, and each 4,4′-tppcp molecule acts as two fused 3-connected vertices, with each vertex of the cyclophane being located at the center of each cyclobutane (cb) ring. Thus, **1** defines a nonregular net of vertex type (4.6^2;4.6.4.6), based on 3- and 4-connected vertices that form alternating rows of square and hexagon cavities. This topology is related to the 2-uniform net of vertex type ($3^2.6^2$;3.6.3.6)[7,15] and is found in the β-W (e.g., Cr_3Si) and garnet structures.[3] A similar topology has also been observed in layered $NEt_4OH \cdot 4H_2O$,[16a] $[N(Me)_4]_8[Si_{24}O_{52}(OH)_4] \cdot 20H_2O$,[16b] and $CF_3COOH \cdot 4H_2O$.[16c]

Scheme 1



Views of the cavities of **1** are shown in Figure 2. The walls of the square cavities (approximate dimensions (Å): 7.2 × 7.4 Å)

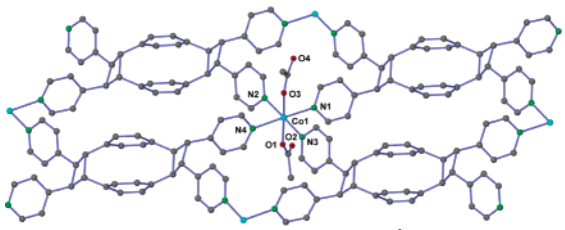


Figure 1. Structure of **1**. Selected bond distances (Å) and angles (°): Co1−O1 2.055(4), Co1−O3 2.032(4), Co1−N1 2.180(6), Co1−N2 2.187(6), Co1−N3 2.200(6), Co1−N4 2.235(6), N1−Co1−N2 93.3(2), N1−Co1−N3 88.8(2), N3−Co1−N4 91.4(2), N2−Co1−N4 86.6(2), N1−Co1−N4 178.0(2), N2−Co1−N3 177.7(2). Co = cyan; C = gray; O = red; N = green.

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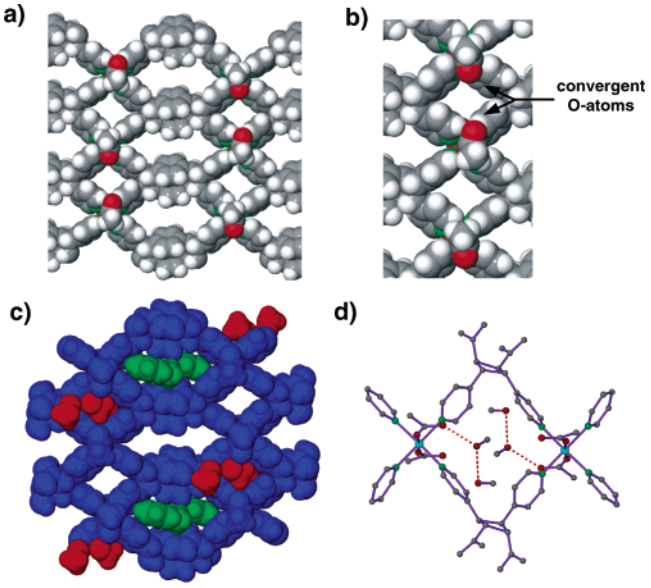

Figure 2. The cavities of **1**: (a) alternating rows of squares and hexagons (Co = cyan; C = gray; H = light gray; O = red; N = green); (b) orientation of the acetate O-atoms; (c) guests (**1** = blue, MeOH = red, toluene = green); and (d) hydrogen bonds (dotted) involving MeOH and square cavities.

are composed of pyridyl groups, while the walls of the hexagon cavities (approximate dimensions (Å): cb···cb 6.4, Co···cb 7.2, Co···Co 17.3) are composed of pyridyl and cyclophane units (Figure 2a). The central rings of the paracyclophane adopt a boat conformation,[10] while the mean plane defined by the two rings is twisted 55° with respect to the plane of the 2D net. The twisting results in the edges of the cyclophane being projected into the hexagon cavities.[17] The free O-atoms of the carboxylate groups converge above and below identical square cavities (Figure 2b), which means that the O-atoms converge above alternating square cavities of each row of squares and offset square cavities of adjacent rows of each grid.

In line with our design, the two different cavities of **1** host two different guests. The guests interact with **1** via either hydrophilic or hydrophobic forces. Specifically, a MeOH molecule and two toluene molecules fill half of the square and half of the hexagon cavities, respectively (Figure 2c). The MeOH molecule, which lies disordered across two positions, participates in an O−H···O hydrogen bond with a free O-atom of a carboxylate (O···O separations (Å): O(2)···O(70A)a 2.60(1), O(4)···O(70B)a 2.95(4); a: $x + 1, y, z$), while the toluene molecules participate in edge-to-face $\pi-\pi$ forces with the cyclophane. A second MeOH molecule is included in **1** and participates in an O−H···O hydrogen bond [O···O separations (Å): O(60A)···O(70A)b 2.86(1)] with the MeOH molecule of the square cavity (Figure 2d). In effect, the MeOH located in the square cavity occupies a binding pocket formed by the two convergent O-atoms of the acetate ions.

The grids of **1** self-organize in an *ABAB* stacking pattern (interlayer separation: 6.1 Å) in which the acetate ions are projected into the corners of the hexagon cavities. A thermal analysis reveals that **1** decomposes in five steps with the two guests being released separately. The first release occurs between 25 and 85 °C and corresponds to MeOH (exp. 7.0%, calcd 7.1%), and the second release occurs between 85 and 225 °C and corresponds to toluene (exp. 9.6%, calcd 10.2%). The remaining steps occur between 255 and 585 °C and are attributed to decomposition of **1** to give Co_2O_3 (exp. 9.4%, calcd 9.2%).

That the components of **1** assemble to form a nonregular net with a structure related to one of the 20 known 2-uniform nets[7] can be ascribed to the ability of the cyclophane to define two fused 3-connected nodes within the framework. Indeed, the number of nets with two or more regular polygons *and* more than one type of vertex is *endless*.[3] This infinite set includes nets, as for **1**, based on 3- and 4-connected nodes. For **1**, the structure of the cyclophane can be considered to, in effect, mitigate against the formation of other possible nets based on 3- and 4-connected vertices by forcing two 3-connected nodes to be fused via covalent linkages. This means that the assembly process is restricted to give a net with two fused 3-connected nodes.[6] Moreover, that the self-assembly process is prone to give a net of high symmetry[6] means that a likely outcome is a nonregular net with a structure that conforms to a uniform net,[18] as with **1**. Having achieved the construction of **1**, we believe this strategy of O'Keeffe and Yaghi, in which an organic molecule codes for fused vertices within a MOF,[6] may be employed to construct additional nets (e.g., *n*-uniform nets) with multiple cavities wherein organic molecules are designed, a priori, to code for specific vertices within targeted framework structures.[6]

In conclusion, we have constructed a MOF with multiple cavities. A [2.2]paracyclophane has defined multiply fused nodes of a 2D net with square and hexagon cavities. We anticipate this approach may be used to generate other MOFs with multiple cavities to aid the design of targeted MOF structures.[1,6]

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Supporting Information Available: Crystallographic reports and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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